THE PREPARATION AND DISTRIBUTION OF

ARGONNE PREMIUM COAL SAMPLES*

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ABSTRACT

The eight Argonne Premium Coal Samples were each collected in about 1 1/2 ton quantities, placed in steel drums, purged with argon and taken to ANL for processing. After transfer to a nitrogen filled enclosure, they were crushed, pulverized, mixed and packaged in sealed amber borosilicate ampoules containing 10 grams of -20 mesh or 5 grams of -100 mesh sample. Five gallon carboys hold about 80% of the batch in reserve for filling more ampoules after the original about 5,000 of -20 mesh or 10,000 of -100 mesh samples are depleted. More than 70 laboratories are participating in the analysis. Over 90 shipments have been made to more than 45 different organizations for a range of programs which will be the subject of later papers in the symposium.

INTRODUCTION

The Premium Coal Sample Program is intended to provide the basic coal research community with the best quality samples of a limited number (8) of coals for basic research. The availability of the ampoules is the result of the cooperation of many individuals within a number of organizations whose efforts made the high quality of the samples possible.

The premium coal samples produced from each coal and distributed through this program are chemically and physically as identical as possible, have well characterized chemical and physical properties, and will be stable over long periods of time. Coals have been mined, transported, processed into the desired particle and sample sizes and packaged in humid nitrogen environments as free of oxygen as possible. The need for a Premium Coal Sample Program was expressed on a number of occasions, culminating in the Coal Sample Bank Workshop held March 27 and 28, 1981 in Atlanta, Georgia.

SELECTION OF THE COALS

Support has been provided by the Office of Basic Energy Sciences

to make eight carefully selected coals available. The selection of these coals was based on those parameters which would repre sent significant differences among the available coals and maxi mize our understanding of the fundamental properties of coal. A cluster analysis was carried out to establish desirable samples in terms of the significant compositional parameters, C, H, O and S. This was augmented by considerations of maceral content, paleobotanic origins, age and coking properties.

IDENTITY OF SAMPLES AND CHARACTERISTICS

The coals are listed in the order collected. Preliminary data describing the samples are given below. The moisture and ash-free values are given in %, except for sulfur and ash which are in dry %.

#	Seam	State	Rank	C	H	O	S	Ash
1	Upper Freeport	PA	Med. Vol. Bit.	87	5.5	4	2.8	13
2	Wyodak-Anderson	WY	Subbituminous	74	5.1	19	0.5	8
3	Illinois #6	IL	High Vol. Bit.	77	5.7	10	5.4	16
4	Pittsburgh (#8)	PA	High Vol. Bit.	83	5.8	8	1.6	9
5	Pocahontas #3	VA	Low Vol. Bit.	91	4.7	3	0.9	5
6	Blind Canyon	UT	High Vol. Bit.	79	6.0	13	0.5	5
7	Lewiston-Stockton	WV	High Vol. Bit.	81	5.5	11	0.6	20
8	Beulah-Zap	ND	Lignite	73	5.3	21	0.8	6

COLLECTION AND TRANSPORTATION OF SAMPLES

The samples were collected from sites selected in cooperation with the U. S. Geological Survey. The USGS provided technical supervision while a special collection crew from the Pittsburgh Testing Laboratory removed the channel-type sample from each of the underground sites. Usually a fresh block of coal about 18" wide, the thickness of the seam and several feet deep was isolated, removed and placed into stainless steel 55 gallon drums. Surface samples were placed directly into the drums. The drums of coal were placed in a semi-trailer within 1-4 hours from the initiation of the sample collection. The drums were then purged with enough argon gas to reduce the oxygen content to 100 ppm by the same truck driver. The drums were pressurized to 5 psi and taken to Argonne National Laboratory at 42°F, usually within 24 hours.

PREPARATION OF SAMPLES

The drums were unloaded from the truck, weighed and placed into an airlock in a nitrogen-filled processing facility. The oxygen content of the facility was maintained below 100 ppm of oxygen, and typically was about 30 ppm. After the airlock was purged, the drums were opened, and the contents were transferred to a crusher, where the sample was reduced to pieces that would pass between bars with openings 1/2" apart. The crushed coal was

elevated to the pulverizer where it was ground to pass a 20 mesh screen. The entire one-ton batch used for processing was ground and accumulated in a 2000 liter mixer-blender. After thorough mixing the sample was transferred by a tubular conveyer to a second enclosure. About half the batch was transferred to special 5 gallon leverlock pails for transfer back to the initial airlock for later repulverizing to -100 mesh. The balance was mostly placed into 5 gallon borosilicate glass carboys for long-term storage. About 5,000 ampoules containing 10 grams of -20 samples were sealed with a hydrogen-oxygen torch. The flame was kept at the stoichiometric composition with a mass flow controller. The half batch that was transferred to the initial airlock was pulverized to pass a 100 mesh screen and accumulated again in the mixer-blender. After mixing the -100 mesh material was transferred to the second enclosure for placing into 5 gallon borosilicate carboys and into 10,000 ampoules of 5 grams of -100 mesh material. The ANL glassblower sealed the carboys for long term storage. Samples were taken during the processing for homogeneity analyses to establish the uniformity of the samples during the processing and sealing.

One of the samples, the Illinois #6, was taken from the same block of coal which was also collected for the Illinois State Geological Survey. That sample is known as the Illinois Basin Coal Sample Program #5. Larger quantities (1 lb to 50 lbs) of that sample may be obtained from the ISGS.

ANALYSIS OF SAMPLES

The homogeneity samples were irradiated and the induced radioactivity of several isotopes was counted to indicate the content of each species in the samples. A high degree of uniformity was found.

Additional samples have been submitted for a range of analyses including: proximate, ultimate, major and minor elements in the ash, heat content, forms of sulfur, maceral analysis, and reflectance measurements. A large number of laboratories is participating in the analytical studies.

In order to establish the long term stability of the samples, additional analytical work is done including the evaluation of the gas atmosphere inside of the ampoules at two month intervals. For the bituminous samples, Gieseler plasticity measurements are being made to establish the fluidity at various intervals. To date, no indications of oxidation or loss of fluidity have been found.

DISTRIBUTION OF SAMPLES

Samples are distributed as 5 gram ampoules of -100 mesh or 10 gram ampoules of -20 mesh material. Shipments typically involve multiples of 6 or 12 ampoules in special cardboard cartons, with

added foam padding to increase the probability of safe arrival. Orders are sent to the Assistant Controller at ANL, and after processing, are filled and shipped by UPS or international air courier. Order forms may be obtained from the author. A nominal charge of $8 (US) is made for the 5 gram ampoules and $16 for the 10 gram ampoules. International shipments involve an additional charge of $20 for a set of six ampoules.

To date over 89 orders have been filled for more than 3,000 ampoules.

Two types of ampoules have become available during processing. Initially the ampoules were of a standard type with a gradually sloping shoulder to the tip. The "easy-break" ampoules became available later and have been used for the latter coal samples. Instructions for opening the ampoules are included with each shipment. Appropriate care must be exercised in the opening to avoid mixing glass fragments in the coal and to protect the hands of the experimenter.

The importance of mixing must be stressed. All coal samples are subject to segregation on standing. It is necessary to remix the sample before opening the ampoule. The recommended method is to turn the ampoule so that the coal alternately falls into the top and then the body of the ampoule. This should be repeated a number of times (at least 10). Rolling the ampoule on its side is not as effective and should not be relied upon for thorough mixing.

The samples are intended to be used immediately after opening. Any unused portion should be discarded, as the original properties may change on further storage.

RESEARCH BEING DONE WITH THE SAMPLES

The types of research being done with the premium samples includes a cross section of the areas of basic and applied coal research. Some major areas include:

Analytical Studies

A number of analytical studies are being carried out. A direct measurement of organic sulfur by examination of a number of individual coal particles by reflected radiation is being developed. The initial results indicate that the sulfur content of a given maceral may be different than the parent coal but is similar from one maceral particle to another particle of the same maceral. A direct measurement of oxygen is being developed by the use of fast neutron activation, and direct counting of the induced oxygen activity. Corrections are made for oxygen present in the moisture and mineral matter. Several groups are working to establish the relative amounts of the different macerals in

the coal and to separate these macerals. Another group is studying the occurrence of sodium and chloride in the coal to establish the forms in which it may be bound. Still others are using some of the newer instruments, such photoacoustic FTIR to understand the functional groups present in the coal and near the surface. Plasma excitation is being studied to establish the species produced by this technique. Trace element geochemistry is being used to evaluate the relative amounts of the trace elements and to correlate the occurrence of these elements with other factors. One researcher is comparing the carbon found in coal with that found in meteorites.

Physical Properties

The heat capacities of the samples over a range of temperatures are being studied with fresh and aged samples. Interesting differences have been found. The pore characteristics are being studied by a variety of techniques. Solvent swelling studies have also been initiated.

Structure Studies

At least six laboratories are using nuclear magnetic resonance techniques to carry out a variety of structural studies. Several of these will be reported later in the symposium. Chemical techniques are being used by at least three different laboratories. Solvent extraction is being used to evaluate the classes of materials which are present and to determine the effects of aging on the relative amounts of these species. Supercritical extraction is being used at three or more laboratories for similar purposes. The nature and amount of acidic sites is the subject of study at two laboratories. Other workers are using alkylation of sites to establish the effects of altering certain classes of functional groups. Two groups are examining the nature of the water in the coal. Other workers are studying the different forms of sulfur present in the samples to establish the organic and inorganic species which are present. In a number of cases the researchers are using a variety of techniques to probe more deeply into the structural features of the coal material.

Coal Conversion

Pyrolysis is being used at seven or more laboratories to release different species and understand the factors involved in the thermally induced changes. Coal desulfurization by a variety of techniques is another popular area of research. Liquefaction is also being studied at three laboratories with these samples. The catalytic effects on coal conversion is also being evaluated.

The Program Manager is also following the progress of small changes in gas composition of the atmosphere in the ampoules as time passes.

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